

PATENT ABSTRACTS OF JAPAN

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(54) HYDROGENATED NITRILE RUBBER COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogenated nitrile rubber composition which is excellent in heat resistance, pressure deflection resistance, abrasion resistance and heat conduction and can be used efficiently as the molding material for a sliding or high pressure sealant.

SOLUTION: The hydrogenated nitrile rubber composition comprises carbon black and the other fillers, wherein the total amount of the carbon black and the other fillers is about 120 parts by weight or more relative to 100 parts by weight of the hydrogenated nitrile rubber having a binding acrylonitrile content of 38% or more, a hydrogenation rate of 90% or more and an iodine value (central value) of 28 or more; and the composition has a thermal conductivity of 0.4 W/m.K or higher at 20°C and can provide a crosslinked product having a 50% modulus of 14 MPa or higher.

LEGAL STATUS

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CLAIMS

[Claim(s)]

[Claim 1] The hydrogenated-nitrile-rubber constituent with which the rate of hydrogenation comes for the amount of acrylonitrile association to blend the carbon black and other bulking agents with which the iodine number (central value) serves as the total quantity more than the about 120 weight section per [which is 28 or less] hydrogenated-nitrile-rubber 100 weight section 90% or more 38% or less, the heat conductivity in 20 degrees C is 0.4 or more W/m-K, and a modulus gives the bridge formation object of 14 or more MPas 50%.

[Claim 2] The hydrogenated-nitrile-rubber constituent according to claim 1 with which the bulking agent which consists of the carbon black about 30 to 100 weight section and the graphite about ten to 80 weight section was used.

[Claim 3] The hydrogenated-nitrile-rubber constituent according to claim 1 with which the bulking agent which consists of the carbon black about 30 to 100 weight section, the graphite about ten to 60 weight section, and the carbon fiber about five to 60 weight section was used.

[Claim 4] The hydrogenated-nitrile-rubber constituent according to claim 1 with which organic peroxide was blended as a cross linking agent.

[Claim 5] The hydrogenated-nitrile-rubber constituent according to claim 1 used as a molding material of a sealant.

[Claim 6] Bridge formation mold goods constructed for which the bridge and obtained in the hydrogenated-nitrile-rubber constituent according to claim 1.

[Claim 7] Bridge formation mold goods according to claim 6 heat-treated at the temperature of about 180 degrees C or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a hydrogenated-nitrile-rubber constituent. Furthermore, it is related with the hydrogenated-nitrile-rubber constituent which can give bridge formation mold goods excellent in thermal resistance, proof-pressure deformans, a wear property, thermal conductivity, etc. in detail.

[0002]

[Description of the Prior Art] Although hydrogenated nitrile rubber is used from the former as a molding material of the various sealants of the outstanding ingredient physical properties and thermal resistance, therefore an absorber seal and others, the further reinforcement is called for these days.

[0003] Generally, the endurance life of a sealant is based on degradation, setting, etc. in a lip part which touch a shaft in many cases, and an endurance life is improvable if degradation and setting in the part are controlled. If thermal resistance and wear-resistant lack of an ingredient, the fall of a compression set-proof property, etc. are mentioned and considering the degradation and cause of setting these can be improved, it will become possible to improve an endurance life sharply.

[0004] Moreover, in the sealant for sliding, generation of heat at the time of sliding also influences a life. Generally, the thermal conductivity of a rubber ingredient is low, and also when only a lip part deteriorates by sliding generation of heat of a sealing surface, there is. Furthermore, for the sealant application for high pressures which fluid pressure and gas pressure, such as oil pressure and water pressure, cut in 1 - 20MPa extent, the proof-pressure deformans to the sealant under high pressure is also called for.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is excellent in thermal resistance, proof-pressure deformans, a wear property, thermal conductivity, etc., and is to offer the hydrogenated-nitrile-rubber constituent which can be effectively used as a molding material of the sealants the object for sliding, for high pressures, etc.

[0006]

[Means for Solving the Problem] The amount of acrylonitrile association comes to blend the carbon black and other bulking agents used as the total quantity per [90% or more and whose iodine number (central value) 38% or less and the rate of hydrogenation are 28 or less] hydrogenated-nitrile-rubber 100 weight section, and more than the about 120 weight section, and, as for the purpose of this this invention, is attained by the hydrogenated-nitrile-rubber constituent with which the heat conductivity in 20 degrees C is 0.4 or more W/m-K, and a modulus gives the bridge formation object of 14 or more MPas 50%.

[0007]

[Embodiment of the Invention] As hydrogenated nitrile rubber, the rate of hydrogenation is used for the amount of acrylonitrile (AN) association, and the thing of 4-28 is preferably used for the iodine number (central value) 28 or less 91% or more 90% or more 17 to 36% 38% or less.

[0008] Although the hydrogenated-nitrile-rubber constituent with which the amount of acrylic nitril association added the thin film integrated circuit bulking agent with the carbon black of a rate which is specified to 36% or less of hydrogenated nitrile rubber by this invention is indicated by JP,8-217919,A, without spoiling a low-temperature property, it aims at giving bridge formation mold goods excellent in gas-proof permeability, and completely differs in the purpose and configuration of invention with this invention there.

[0009] In this invention, although thermal conductivity is good if the amount of acrylonitrile association is made into 38% or more, it is inferior to thermal resistance and a wear property, and only the big bridge formation mold goods of especially sliding generation of heat are obtained. Moreover, the rate of hydrogenation is also the same as when less than 90% of hydrogenated nitrile rubber is used, and the iodine number (central value) is also limited or less with 28 corresponding to this.

[0010] The carbon black and other bulking agents which serve as the total quantity more than the about 120 weight section per 100 weight sections of that are blended with the hydrogenated nitrile rubber which has this description, and it is used for it. If there is less total quantity of the bulking agent added than this, it will no longer be satisfied in respect of a wear property or thermal conductivity. What consists of the thing which consists of the carbon black about 30 to 100 weight section and the graphite about ten to 80 weight section or the carbon black about 30 to 100 weight section, the graphite about ten to 60 weight section, and the carbon fiber about five to 60 weight section as combination of desirable carbon black and other bulking agents is mentioned. As carbon black, carbon black, such as SRF and HAF, is used and a desired improvement is not attained only in carbon black at the **** case for the specified quantity in respect of any of thermal resistance, a wear property, and thermal conductivity. What is generally marketed is used as graphite and especially addition of that is effective in an improvement of a wear property and thermal conductivity. Moreover, a wear property is made to improve further, when the thing whose diameter of fiber is about 1-20 micrometers and whose fiber length it is carbon fibers, such as a pitch system and a PAN system, and is about 0.03-1mm as a carbon fiber is generally used and uses together with graphite.

[0011] As other bulking agents other than these, a silica, talc, clay, polytetrafluoroethylene powder, activated carbon acid calcium, silicic-acid calcium, etc. are mentioned, for example. When using a silica, it is desirable to use a silane coupling agent etc. together for the improvement of reinforcement nature. Moreover, when polytetrafluoroethylene powder is added, the further lubricative improvement is expected.

[0012] Although the wear property is made to improve by using together carbon black and cross-linking radical content acrylic rubber in the former although the hydrogenated-nitrile-rubber constituent which added the carbon black of the about 20 to 150 weight section or the reinforcing agent of the about 20 to 180 weight section per hydrogenated-nitrile-rubber 100 weight section, respectively is well-known respectively (JP,2-132135,A, 9-132675 official report), there is no reference about thermal resistance and thermal conductivity, and the latter is turned to amelioration of chlorofluocarbon-proof nature.

[0013] Generally peroxide bridge formation of the hydrogenated-nitrile-rubber constituent which consists of each above component is carried out using organic peroxide. As organic peroxide, for example II tertiary butyl peroxide, dicumyl peroxide, Tertiary butyl cumyl peroxide, 1, and 1-II (the 3rd butylperoxy) - 3, 3, a 5-trimethyl cyclohexane, 2, the 5-dimethyl -2, 5-II (3rd butylperoxy) hexane, 2, the 5-dimethyl -2, 5-II (3rd butylperoxy) hexyne - 3, 1, 3-II (3rd butylperoxy isopropyl) benzene, 2, the 5-dimethyl -2, 5-II (benzoylperoxy) hexane,

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a hydrogenated-nitrile-rubber constituent. Furthermore, it is related with the hydrogenated-nitrile-rubber constituent which can give bridge formation mold goods excellent in thermal resistance, proof-pressure deformans, a wear property, thermal conductivity, etc. in detail.

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PRIOR ART

[Description of the Prior Art] Although hydrogenated nitrile rubber is used from the former as a molding material of the various sealants of the outstanding ingredient physical properties and thermal resistance, therefore an absorber seal and others, the further reinforcement is called for these days.

[0003] Generally, the endurance life of a sealant is based on degradation, setting, etc. in a lip part which touch a shaft in many cases, and an endurance life is improvable if degradation and setting in the part are controlled. If thermal resistance and wear-resistant lack of an ingredient, the fall of a compression set-proof property, etc. are mentioned and considering the degradation and cause of setting these can be improved, it will become possible to improve an endurance life sharply.

[0004] Moreover, in the sealant for sliding, generation of heat at the time of sliding also influences a life. Generally, the thermal conductivity of a rubber ingredient is low, and also when only a lip part deteriorates by sliding generation of heat of a sealing surface, there is. Furthermore, for the sealant application for high pressures which fluid pressure and gas pressure, such as oil pressure and water pressure, cut in 1 - 20MPa extent, the proof-pressure deformans to the sealant under high pressure is also called for.

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EFFECT OF THE INVENTION

[Effect of the Invention] The hydrogenated-nitrile-rubber constituent concerning this invention is excellent in thermal resistance, proof-pressure deformans, and a wear property, and since the thermal conductivity in 20 degrees C not only also indicates a good value to be 0.4 or more W/m-K, but the bridge formation mold goods to which the calorific value at the time of sliding can also be reduced sharply are given, it is effectively used as a molding material of the object for sliding, or the sealant for high pressures etc.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention is excellent in thermal resistance, proof-pressure deformans, a wear property, thermal conductivity, etc., and is to offer the hydrogenated-nitrile-rubber constituent which can be effectively used as a molding material of the sealants the object for sliding, for high pressures, etc.

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MEANS

[Means for Solving the Problem] The amount of acrylonitrile association comes to blend the carbon black and other bulking agents used as the total quantity per [90% or more and whose iodine number (central value) 38% or less and the rate of hydrogenation are 28 or less] hydrogenated-nitrile-rubber 100 weight section, and more than the about 120 weight section, and, as for the object of this invention, is attained by the hydrogenated-nitrile-rubber constituent with which the heat conductivity in 20 degrees C is 0.4 or more W/m-K, and a modulus gives the bridge formation object of 14 or more MPas 50%.

[0007]

[Embodiment of the Invention] As hydrogenated nitrile rubber, the rate of hydrogenation is used for the amount of acrylonitrile (AN) association, and the thing of 4-28 is preferably used for the iodine number (central value) 28 or less 91% or more 90% or more 17 to 36% 38% or less.

[0008] Although the hydrogenated-nitrile-rubber constituent with which the amount of acrylic nitril association added the thin film integrated circuit bulking agent with the carbon black of a rate which is specified to 36% or less of hydrogenated nitrile rubber by this invention is indicated by JP,8-217919,A, without spoiling a low-temperature property, it aims at giving bridge formation mold goods excellent in gas-proof permeability, and completely differs in the object and configuration of invention with this invention there.

[0009] In this invention, although thermal conductivity is good if the amount of acrylonitrile association is made into 38% or more, it is inferior to thermal resistance and a wear property, and only the big bridge formation mold goods of especially sliding generation of heat are obtained. Moreover, the rate of hydrogenation is also the same as when less than 90% of hydrogenated nitrile rubber is used, and the iodine number (central value) is also limited or less with 28 corresponding to this.

[0010] The carbon black and other bulking agents which serve as the total quantity more than the about 120 weight section per 100 weight sections of that are blended with the hydrogenated nitrile rubber which has this description, and it is used for it. If there is less total quantity of the bulking agent added than this, it will no longer be satisfied in respect of a wear property or thermal conductivity. What consists of the thing which consists of the carbon black about 30 to 100 weight section and the graphite about ten to 80 weight section or the carbon black about 30 to 100 weight section, the graphite about ten to 60 weight section, and the carbon fiber about five to 60 weight section as combination of desirable carbon black and other bulking agents is mentioned. As carbon black, carbon black, such as SRF and HAF, is used and a desired improvement is not attained only in carbon black at the **** case for the specified quantity in respect of any of thermal resistance, a wear property, and thermal conductivity. What is generally marketed is used as graphite and especially addition of that is effective in an improvement of a wear property and thermal conductivity. Moreover, a wear property is made to improve further, when the thing whose diameter of fiber is about 1-20 micrometers and whose fiber length it is carbon fibers, such as a pitch system and a PAN system, and is about 0.03-1mm as a carbon fiber is generally used and uses together with graphite.

[0011] As other bulking agents other than these, a silica, talc, clay, polytetrafluoroethylene powder, activated carbon acid calcium, silicic-acid calcium, etc. are mentioned, for example. When using a silica,

it is desirable to use a silane coupling agent etc. together for the improvement of reinforcement nature. Moreover, when polytetrafluoroethylene powder is added, the further lubricative improvement is expected.

[0012] Although the wear property is made to improve by using together carbon black and cross-linking radical content acrylic rubber in the former although the hydrogenated-nitrile-rubber constituent which added the carbon black of the about 20 to 150 weight section or the reinforcing agent of the about 20 to 180 weight section per hydrogenated-nitrile-rubber 100 weight section, respectively is well-known respectively (JP,2-132135,A, 9-132675 official report), there is no reference about thermal resistance and thermal conductivity, and the latter is turned to amelioration of chlorofluocarbon-proof nature.

[0013] Generally peroxide bridge formation of the hydrogenated-nitrile-rubber constituent which consists of each above component is carried out using organic peroxide. As organic peroxide, for example II tertiary butyl peroxide, dicumyl peroxide, Tertiary butyl cumyl peroxide, 1, and 1-II (the 3rd butylperoxy) - 3, 3, a 5-trimethyl cyclohexane, 2, the 5-dimethyl -2, 5-II (3rd butylperoxy) hexane, 2, the 5-dimethyl -2, 5-II (3rd butylperoxy) hexyne - 3, 1, 3-II (3rd butylperoxy isopropyl) benzene, 2, the 5-dimethyl -2, 5-II (benzoylperoxy) hexane, the 3rd butylperoxy benzoate, the 3rd butylperoxyisopropyl, n-butyl -4, 4'-II (3rd butylperoxy) valerate, etc. -- per hydrogenated-nitrile-rubber 100 weight section -- the about one to 10 weight section -- it is preferably used at a rate of the about two to 8 weight section.

[0014] When organic peroxide is used, it is desirable that a polyfunctional unsaturated compound is used together, for example, a triaryl (ISO) SHIANU rate, TORIMECHI roll pro pantry (meta) acrylate, triallyl trimellitate, etc. are used.

[0015] Into a constituent, further, in rubber industry, such as carrier acid, such as processing aid, such as stearin acid, a palmitic acid, and paraffin wax, a zinc oxide, and a magnesium oxide, an antioxidant, and a plasticizer, it is added suitably and the various compounding agents generally used are used.

[0016] Preparation of a constituent is performed by kneading using a kneading machine or opening rolls, such as INTAMIKKUSU, a kneader, and a Banbury mixer, etc., the bridge formation is performed using an injection molding machine, a compacting machine, the vulcanizing press, etc. by generally carrying out grade heating for about 3 - 60 minutes at about 160-220 degrees C, and heat-treatment further heated above about 180 degrees C for about 1 to 30 hours if needed is also performed. Moreover, such heat-treatment is effective also in thermal resistance or the further pressure-resistant improvement.

[0017] Thus, 0.4 or more W/m-K of thermal conductivity in 20 degrees C is 0.5 or more W/m-K preferably, and the constituent over which a bridge is constructed gives the bridge formation object whose modulus is 14 or more MPas 50%. Generally, although it is low, if thermal conductivity becomes high, the thermal conductivity of a rubber ingredient becomes easy to radiate heat in sliding-surface generation of heat at the time of sliding, and is advantageous in respect of thermal resistance. Moreover, the value with high 50% modulus is advantageous in respect of proof-pressure deformans. That is, although a lip configuration etc. deforms with a pressure under high voltage, a deformation degree becomes small, so that this value is large.

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EXAMPLE

[Example] Next, this invention is explained about an example.

[0020]

Example 1 Hydrogenation NBR (whenever [36.2% / of the amounts of Nippon Zeon product ZETT pole 2000;AN(s) /, and 100 weight section hydrogenation] 99.5%, the iodine number 4, Mooney viscosity 85)

SRF carbon black 90 ** graphite (Japanese ** carbon product AO) 30 ** antioxidant (uni-royal company product 445) 2 ** organic peroxide (Nippon Oil & Fats product Park Mill D) Each component more than 6 ** was kneaded with a 10 inch roll, press bridge formation of this was carried out for 3 minutes at 180 degrees C, and the test piece with a thickness of 2mm was fabricated.

[0021] Each following item was measured using this test piece.

ordinary state physical-properties: -- JIS K-6251 conformity heatproof aging nature: -- as the elongation change after 175 degrees C and the air oven aging test of 70 hours -- the bottom of the pin made from measurement wear property:partner material S45C, the linear velocity of 1m/second, 10 Ns of loads, and desiccation conditions -- the sliding calorific value and abrasion loss for [sliding time amount] 20 minutes -- a 30x30cm test piece -- thermal-conductivity-measuring-apparatus ARC-TC -1 made from measurement thermal conductivity:AGUNE -- using -- the bottom of room temperature conditions (20 degrees C) -- measurement [0022] The amount of graphite was changed into 60 weight sections in example 2 example 1.

[0023] In example 3 example 1, further, the carbon fiber (Osaka Gas chemical product pitch system carbon fiber; diameter [of 10 micrometers] of fiber, fiber length of 0.06mm) 30 weight section added, and was used.

[0024] In example of comparison 1 example 1, graphite was not used but the amount of SRF carbon black was changed into 80 weight sections.

[0025]

Example 4 Hydrogenation NBR (whenever [36.2% / of the amounts of Nippon Zeon product ZETT pole 2010;AN(s) /, and 100 weight section hydrogenation] 96%, the iodine number 11, Mooney viscosity 85)

SRF carbon black 60 ** silica (Japanese silica product nip seal ER) 30 ** graphite (Japanese ** carbon product AO) 30 ** PTFE powder (Kitamura product KTL-8N) 15 ** silane coupling agent (Nippon Unicar product A172) 1 ** antioxidant (uni-royal company product 445) 2 ** organic peroxide (Park Mill D) Kneading, bridge formation, and measurement were performed like the example 1 using each component more than 6 **.

[0026]

Example 5 Hydrogenation NBR (ZETT pole 2010) The 100 weight sections SRF carbon black 90 ** graphite (Japanese ** carbon product AO) 60 ** antioxidant (uni-royal company product 445) 2 ** organic peroxide (Park Mill D) Using each component more than 6 **, like the example 1, after kneading and press constructing a bridge, oven bridge formation (secondary bridge formation) of 10 hours was performed at 180 degrees C, and same measurement was performed about this test piece.

[0027] It sets in the example of comparison 2 example 2, and the Nippon Zeon product ZETT pole 2030 (whenever [36.2% / of the amounts of AN(s) / and hydrogenation]% [83 - 85], the iodine number 56, Mooney viscosity 57.5) is ***** for tales doses as hydrogenation NBR.

[0028] It sets in the example of comparison 3 example 2, and the Nippon Zeon product ZETT pole 1020 (whenever [44.2% / of the amounts of AN(s) / and hydrogenation]% [91], the iodine number 24, Mooney viscosity 78) is ***** for tales doses as hydrogenation NBR.

[0029] The result obtained in the above each example and example of a comparison is shown in the following table.

A table A parameter Fruit -1 Fruit -2 Fruit -3 Ratio -1 Fruit -4 Fruit -5 Ratio -2 Ratio-3 ordinary-state physical properties Tensile strength (MPa) 31.6 30.5 22.5 33.0 27.5 26.0 28.2 29.8 50% modulus (MPa) 14.2 16.4 17.1 13.1 15.2 18.6 15.5 18.3 Elongation (%) 160 125 95 178 130 72 131 108 heatproof aging nature Elongation change (%) -22 -18 -12 -32 -16 -9 -40 -27 wear property Sliding generation of heat (**T) 84 82 78 118 86 78 108 110 Abrasion loss (cm3) 0.03 0.02 0.01 0.11 0.03 0.01 0.04 0.05 thermal conductivity Under a room temperature condition (W/m-K) 0.52 0.58 0.58 0.36 0.42 0.60 0.58 0.59

[0030] The following can say from the above result.

(1) Each thing of each example shows good thermal resistance, proof-pressure deformans, a wear property, and thermal conductivity, and what constructed the bridge secondarily shows the still better property.

(2) The example 1 for 80phrs of a ***** comparison is inferior to each of these properties only in carbon black.

(3) The example 2 of a comparison for which less than 90% of hydrogenation NBR was used is inferior to thermal resistance and a wear property in whenever [hydrogenation].

(4) The example 3 of a comparison for which 38% or more of hydrogenation NBR was used is also inferior to thermal resistance and a wear property in the amount of CN(s) too.

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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
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[Procedure amendment]
 [Filing Date] August 9, Heisei 14 (2002. 8.9)

[Procedure amendment 1]
 [Document to be Amended] Description
 [Item(s) to be Amended] Claim 1
 [Method of Amendment] Modification
 [Proposed Amendment]

[Claim 1] The hydrogenated-nitrile-rubber constituent with which the rate of hydrogenation comes for the amount of acrylonitrile association to blend the carbon black and other bulking agents with which the iodine number (central value) serves as the total quantity more than the about 110 weight section per [which is 28 or less] hydrogenated-nitrile-rubber 100 weight section 90% or more 38% or less, the heat conductivity in 20 degrees C is 0.4 or more W/m-K, and a modulus gives the bridge formation object of 14 or more MPas 50%.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0006

[Method of Amendment] Modification

[Proposed Amendment]

[0006]

[Means for Solving the Problem] The amount of acrylonitrile association comes to blend the carbon black and other bulking agents used as the total quantity per [90% or more and whose iodine number (central value) 38% or less and the rate of hydrogenation are 28 or less] hydrogenated-nitrile-rubber 100 weight section, and more than the about 110 weight section, and, as for the object of this this invention, is attained by the hydrogenated-nitrile-rubber constituent with which the heat conductivity in 20 degrees C is 0.4 or more W/m-K, and a modulus gives the bridge formation object of 14 or more MPas 50%.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0010

[Method of Amendment] Modification

[Proposed Amendment]

[0010] The carbon black and other bulking agents which serve as the total quantity more than the about 110 weight section per 100 weight sections of that are blended with the hydrogenated nitrile rubber which has this description, and it is used for it. If there is less total quantity of the bulking agent added than this, it will no longer be satisfied in respect of a wear property or thermal conductivity. What consists of the thing which consists of the carbon black about 30 to 100 weight section and the graphite about ten to 80 weight section or the carbon black about 30 to 100 weight section, the graphite about ten to 60 weight section, and the carbon fiber about five to 60 weight section as combination of desirable carbon black and other bulking agents is mentioned. As carbon black, carbon black, such as SRF and HAF, is used and a desired improvement is not attained only in carbon black at the **** case for the specified quantity in respect of any of thermal resistance, a wear property, and thermal conductivity. What is generally marketed is used as graphite and especially addition of that is effective in an improvement of a wear property and thermal conductivity. Moreover, a wear property is made to improve further, when the thing whose diameter of fiber is about 1-20 micrometers and whose fiber length it is carbon fibers, such as a pitch system and a PAN system, and is about 0.03-1mm as a carbon fiber is generally used and uses together with graphite.

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